All types of SBR use compounding recipes, as do other unsaturated hydrocarbon polymers that share the common ingredients of sulfur, accelerators, antioxidants, antiozonants, activators, fillers, and softeners or extenders. SBR requires less sulfur than natural rubber for curing. The usual range is 1.5–2.0 phr of sulfur; however, this range should be based on the rubber hydrocarbon only for oil-extended SBR. Because of their lower unsaturation, all styrene–butadiene rubbers are slower curing than natural rubber and require more acceleration. Processing SBR compounds is similar to that of natural and polybutadiene rubbers. The ingredients are mixed in internal mixers or on mills and may be extruded, calendered, molded and cured in conventional equipment.

## Uses

About 65% of all SBR elastomer produced in the United States is used in the manufacture of passenger-car tires. Two expanding markets for SBR are adhesives (qv) and chewing gum. A wide variety of SBRs is available for adhesive applications, and several of the crumb forms were designed specifically for the adhesives industry.

The block styrene copolymers are intended for applications in adhesives, caulks, sealants, coatings, food packaging, toys, tubing, sheeting, molding equipment, belting, shoe soles and heels, and miscellaneous uses.

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The Goodyear Tire & Rubber Company

S.S. Medvedev, *International Symposium on Macromolecular Chemistry*, Pergamon Press, New York, 1959, pp. 174–190.

# THERMOPLASTIC ELASTOMERS

Thermoplastic resins are polymeric structures that soften or melt at elevated temperatures, allowing them to be processed into fabricated products that, when cooled, recover the physical and chemical properties of the original resin. Of the three classes of thermoplastic elastomers to be discussed, the styrene–diene block copolymers are the largest volume (> 60,000 metric tons), the thermoplastic polyurethanes are next (> 15,000 t), and copolyester ethers, the newest entry, are now > 2000 t.

## Styrene–Diene Thermoplastic Block Copolymers

Preparation of styrene–diene block copolymers is achieved by forming a living polymer, a term coined to describe the product of a polymerization that has no termination or chain-transfer reactions. Shown in Table 1 is a comparison of mechanical properties of SBS block copolymers with vulcanized SBR and natural rubber illustrating the range inherent in the thermoplastic elastomers.

The chemical characteristics of the copolymers are determined by the nature of the components. Alteration of the chemical characteristics is achieved by altering one or more of the blocks.

The styrene–diene thermoplastic elastomers have excellent resistance to water, acids, and bases. Resistance to hydrocarbons, solvents, and oils is poor. The thermoplastic nature limits their utility to temperatures below 65°C depending on the stress. Elastic recovery, compression set, and creep properties are usually inferior to the chemically cross-linked elastomers.

Table 1. Typical Properties of ABA Thermoplastic Elastomers and Conventional Rubbers

| | Kraton 1101[a] | Kraton 1107[b] | Natural rubber | SBR rubber |
|---|---|---|---|---|
| styrene, % | 30 | 14 | | |
| tensile strength, MPa[c] | 31.8 | 21.4 | 20.8 | 14.5 |
| modulus at 300% ext, MPa[c] | 2.8 | 0.7 | 3.5 | 2.1 |
| elongation at break, % | 880 | 1300 | 600 | 800 |
| hardness, Shore A | 71 | 37 | 55 | 45 |
| specific gravity | 0.94 | 0.92 | | |

[a] SBS (styrene–butadiene–styrene).
[b] SIS (styrene–isoprene–styrene).
[c] To convert MPa to psi, multiply by 145.

Table 2. Typical Properties of Segmented Polyether Esters

| 4GT hard segment, % | 33 | 58 | 76 |
|---|---|---|---|
| polymer melt temperature (by dsc[a]), °C | 176 | 202 | 212 |
| specific gravity | 1.15 | 1.20 | 1.22 |
| tensile strength, MPa (psi) | 39.3 (5700) | 44.1 (6400) | 47.5 (6900) |
| elongation at break, % | 810 | 760 | 510 |
| flexural modulus, MPa (psi) | 44.8 (6500) | 206 (30,000) | 496 (72,000) |
| oil swell (ASTM NO. 3 oil, 7 days at 100°C), % vol increase | 22.0 | 12.2 | 6.6 |

[a] Differential scanning calorimetry.

The SBS elastomers may be processed by a wide variety of techniques including solution processing, extrusion, calendering, injection molding, blow molding, and vacuum forming. Standard rubber and plastics equipment is useful for processing the elastomers.

Uses for the thermoplastic elastomers fall into two main sectors: primary raw materials for rubber products without vulcanization, and modifiers to upgrade the qualities of the rubbers and plastics. The largest markets for the styrene–diene block copolymers are footwear, adhesives (qv), and mechanical goods.

### Thermoplastic Urethane Elastomers

Thermoplastic polyurethane (TPU) elastomers are a special class of urethanes that can be processed as plastics and as cements for a wide range of applications (see Urethane polymers). Generally, polyester-based materials are selected for high strength, tear, chemical and heat resistance, and polyether-based materials are selected for low temperature flexibility, high humidity conditions, and resistance to attack by fungi and bacteria.

Since urethane elastoplastics incorporate exceptional resistance to abrasion, fuel and oils, and have high tensile, tear- and load-bearing properties, and are available in a broad durometer range, they are candidates for demanding applications in such areas as automotive, sporting, general mechanical goods, fabric coatings, and biomedical applications such as intra-aortic balloons (see Prosthetic and biomedical devices).

### Thermoplastic Copolyester–Ether Elastomers

Segmented copolyester–ethers represent a novel family of commercial thermoplastic elastomers derived from terephthalic acid (T), polytetramethylene ether glycol (PTMEG), and 1,4-butanediol. They offer an unusual combination of easy processing and high performance under environmental extremes (see Polyesters; Polyethers). The polyester–ether copolymers are prepared by titanate ester (tetrabutyl titanate)-catalyzed melt transesterification of a mixture of dimethyl terephthalate, polyether glycol, and excess 1,4-butanediol. Some typical physical properties are listed in Table 2.

The thermoplastic copolyester–ether elastomers commercialized as Hytrel by DuPont can be processed by injection, blow, compression, transfer, or rotational molding. Some of the many uses of these elastomers include as a replacement for cured rubber and rubber-metal parts with a one-component elastomer unit.
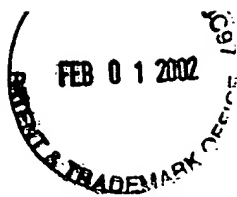
A.F. FINELLI
R.A. MARSHALL
D.A. CHUNG
The Goodyear Tire and Rubber Co.

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KIRK-OTHMER

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## FOURTH EDITION

### VOLUME 9

ELASTOMERS, POLYISOPRENE
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# ELASTOMERS, SYNTHETIC-STYRENE–BUTADIENE RUBBER. See STYRENE–BUTADIENE RUBBER.

## THERMOPLASTIC ELASTOMERS

Thermoplastic elastomers (TPE) were introduced in the 1960s. They have shown rapid growth since then and have been the subject of many conferences, symposia, etc. In particular, the developments in this field have been covered fairly recently in two books: one dealing primarily with the scientific aspects of these polymers (1) and the other dealing primarily with their applications (2). Thermoplastic elastomers have many of the physical properties of rubbers, ie, softness, flexibility, and resilience; but in contrast to conventional rubbers, they are processed as thermoplastics. Rubbers must be cross-linked to give useful properties. In the terminology of the plastics industry, vulcanization is a thermosetting process. Like other thermosetting processes, it is slow and irreversible and takes place upon heating. With thermoplastic elastomers, on the other hand, the transition from a processible melt to a solid, rubberlike object is rapid and reversible and takes place upon cooling. Thermoplastic elastomers can be processed using conventional plastics techniques, such as injection molding and extrusion; scrap is usually recycled.

Because of increased production and the lower cost of raw material, thermoplastic elastomeric materials are a significant and growing part of the total polymers market. World consumption in 1995 is estimated to approach 1,000,000 metric tons (3). However, because the melt to solid transition is reversible, some properties of thermoplastic elastomers, eg, compression set, solvent resistance, and resistance to deformation at high temperatures, are usually not as good as those of the conventional vulcanized rubbers. Applications of thermoplastic elastomers are, therefore, in areas where these properties are less important, eg, footwear, wire insulation, adhesives, polymer blending, and not in areas such as automobile tires.

The classification given in Table 1 is based on the process, ie, thermosetting or thermoplastic, by which polymers in general are formed into useful articles and on the mechanical properties, ie, rigid, flexible, or rubbery, of the final product. All commercial polymers used for molding, extrusion, etc, fit into one of these six classifications; the thermoplastic elastomers are the newest.

**Table 1.** Classification of Polymers According to Properties and Processing

| Property | Thermoset | Thermoplastic |
|---|---|---|
| rigid | epoxy, melamine–formaldehyde, sheet molding compounds | polypropylene, high density polyethylene, polystyrene |
| flexible | highly vulcanized rubber | low density polyethylene, ethylene–vinyl, acetate copolymer, plasticized PVC |
| rubbery | vulcanized rubber | thermoplastic rubbers |

## Structure

Thermoplastic elastomers are often multiphase compositions in which the phases are intimately dispersed. In many cases, the phases are chemically bonded by block or graft copolymerization. In others, a fine dispersion is apparently sufficient. In these multiphase systems, at least one phase consists of a material that is hard at room temperature but becomes fluid upon heating. Another phase consists of a softer material that is rubberlike at RT. A simple structure is an A–B–A block copolymer, where A is a hard phase and B an elastomer, eg, poly(styrene-*b*-elastomer-*b*-styrene).

Most polymer pairs are thermodynamically incompatible and mixtures separate into two phases. This is true even when the polymeric species are part of the same molecule, as in these block copolymers. Poly(styrene-*b*-elastomer-*b*-styrene) copolymers, in which the elastomer is the main constituent, should have a structure similar to that shown in Figure 1. Here, the polystyrene end segments form separate spherical regions, ie, domains, dispersed in a continuous elastomer phase. Most of the polymer molecules have end polystyrene segments in different domains. At RT, these polystyrene domains are hard and act as physical crosslinks, tying the elastomer chains together in a three-dimensional network. In
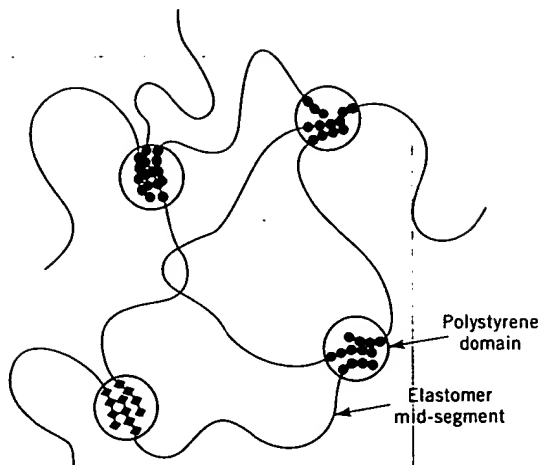
Fig. 1. Phase arrangement in styrenic block copolymers.

some ways, this is similar to the network formed by vulcanizing conventional rubbers using sulfur cross-links. The main difference is that in thermoplastic elastomers the domains lose their strength when the material is heated or dissolved in solvents. This allows the polymer or its solution to flow. When the material is cooled down or the solvent is evaporated, the domains harden and the network regains its original integrity. This explanation of the properties of thermoplastic elastomers has been given in terms of a poly(styrene-*b*-elastomer-*b*-styrene) block copolymer, but it would apply to any block copolymer with the structure A–B–A or (A–B)$_n$. In principle, A can be any polymer normally regarded as a hard thermoplastic, eg, polystyrene, poly(methyl methacrylate), or polypropylene, and B can be any polymer normally regarded as elastomeric, eg, polyisoprene, polybutadiene, polyisobutylene, or polydimethylsiloxane (Table 2).

Block copolymers with structures such as A–B or B–A–B are not thermoplastic elastomers, because for a continuous network to exist both ends of the elastomer segment must be immobilized in the hard domains. Instead, they are much weaker materials resembling conventional unvulcanized synthetic rubbers (4).

Five block copolymers are of commercial importance: poly(styrene-*b*-elastomer-*b*-styrene), thermoplastic polyurethanes, thermoplastic polyesters, thermoplastic polyamides, and polyetherimide–polysiloxane block copolymers. All but the first have the multiblock (A–B)$_n$ structure. The morphology of the polyurethane, polyester, and polyamide block copolymers is shown diagramatically in Figure 2. It has some similarities to that of poly(styrene-*b*-elastomer-*b*-styrene) equivalents (Fig. 1) and also some important differences: (*1*) the hard domains are more interconnected; (*2*) they are crystalline; and (*3*) these long (A–B)$_n$ molecules may run through several hard and soft phases. The polyetherimide–polysiloxane block copolymers share some features of both types. As in the poly(styrene-*b*-elastomer-*b*-styrene) analogues, their hard domains are amorphous. However, these polymers have (A–B)$_n$ structure rather than A–B–A, and so again, each molecule may run through several hard and soft phases.

**Table 2.** Thermoplastic Block Copolymers

| Hard segment, A | Soft or elastomeric segment, B | Structure | Refs. |
|---|---|---|---|
| polystyrene | polybutadiene, polyisoprene | A–B–A | 4–6 |
| poly(α-methylstyrene) | polybutadiene, polyisoprene | A–B–A | 7 |
| polystyrene | poly(ethylene-co-butylene) | A–B–A | 5,6 |
| polyethylene | poly(ethylene-co-butylene) | A–B–A | 7 |
| polystyrene | polydimethylsiloxane | A–B–A | 8 |
| poly(α-methylstyrene) | polydimethylsiloxane | A–B–A and (A–B)$_n$ | 7,8 |
| polysulfone | polydimethylsiloxane | (A–B)$_n$ | 9 |
| poly(silphenylene siloxane) | polydimethylsiloxane | (A–B)$_n$ | 10 |
| polyurethane | polyester or polyether | (A–B)$_n$ | 11–13 |
| polyester | polyether | (A–B)$_n$ | 14,15 |
| polyamide | polyester or polyether | (A–B)$_n$ | 16–18 |
| polycarbonate | polydimethylsiloxane | (A–B)$_n$ | 19–21 |
| polycarbonate | polyether | (A–B)$_n$ | 22,23 |
| polyetherimide | polydimethylsiloxane | (A–B)$_n$ | 24 |
| polystyrene | polyisobutylene | A–B–A | 25 |
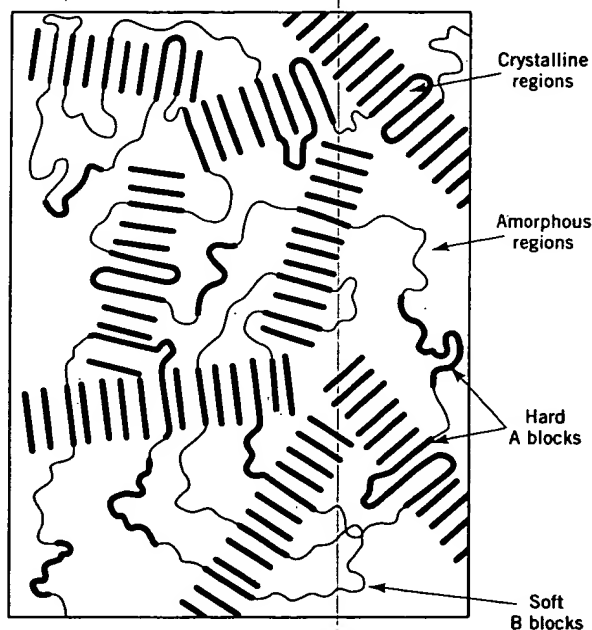


**Fig. 2.** Phase arrangement in crystalline block copolymers.

Not all thermoplastic elastomers are block copolymers. Those that are not are usually combinations of a hard thermoplastic with a softer, more rubberlike polymer. Usually, the components are mechanically mixed together, although it is sometimes possible to produce the rubber component *in situ* during polymerization (26). Typically, the two components form interdispersed multiphase sys-

tems and a diagrammatic structure for blends of this type is shown in Figure 3. Blends of polypropylene with ethylene–propylene–diene monomer (EPDM) were the first materials of this type (27,28). Blends with ethylene–propylene copolymer (EPR) are now more important commercially, and propylene copolymers often replace polypropylene homopolymer as the hard phase. However, some combinations of a hard thermoplastic with a rubberlike polymer are claimed to be single-phase systems (29). In some cases, the elastomer phase is cross-linked while the mixture is being highly sheared (30,31). This process is often referred to as "dynamic vulcanization" (32) and gives a finely dispersed and cross-linked elastomer phase (Fig. 4.).

Other thermoplastic elastomer combinations, in which the elastomer phase may or may not be cross-linked, include blends of polypropylene with nitrile (30,31), butyl (33), and natural (34) rubbers, blends of PVC with nitrile rubber (35,36), and blends of halogenated polyolefins with ethylene interpolymers (29). Collectively, thermoplastic elastomers of this type are referred to herein as hard polymer/elastomer combinations. Some of the more important examples of the various types are shown in Table 3.
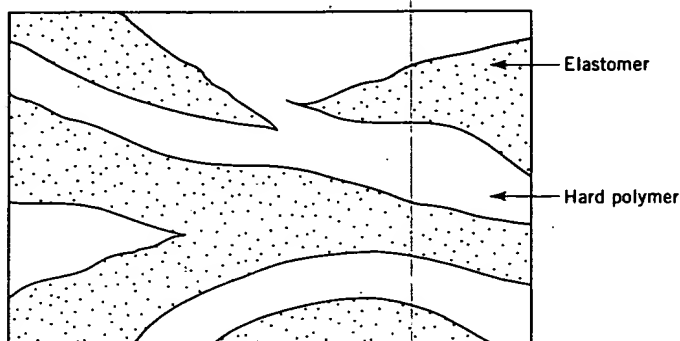


**Fig. 3.** Phase arrangement in hard polymer/elastomer blends.
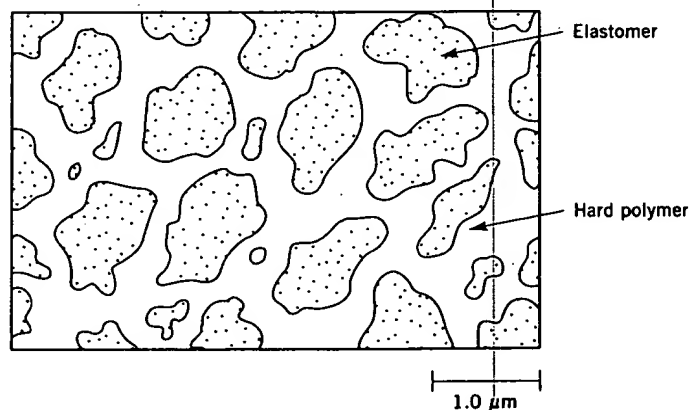


1.0 μm

**Fig. 4.** Phase arrangement in hard polymer/elastomer combinations in which the elastomer phase has been dynamically vulcanized.

**Table 3. Hard Polymer/Elastomer Combinations**

| Hard polymer | Elastomer | Structure[a] | Refs. |
|---|---|---|---|
| polypropylene | EPDM or EPR | B | 27,28 |
| polypropylene | EPDM | DV | 30,31 |
| polypropylene | butyl rubber | DV | 33 |
| polypropylene | natural rubber | DV | 34 |
| polypropylene | nitrile rubber | DV | 30,31 |
| PVC | nitrile rubber | B and DV | 35,36 |
| halogenated polyolefin | ethylene interpolymer | B | 29 |

[a]B = Blend of the two components (27); DV = dynamically vulcanized product in which the elastomer has been cross-linked during mixing (30).

Thermoplastic elastomers based on blends of a silicone rubber (cross-linked during processing) with block copolymer thermoplastic elastomers have also been described (37,38).

## Property–Structure Relationships

Effects of variations in the structure of styrenic A–B–A block copolymers and similar materials were described in early work (4) and have been reviewed (5).

**Molecular Weight.** Compared with homopolymers of similar molecular weight, styrenic block copolymers have very high melt viscosities which increase with increasing molecular weight. These effects are attributed to the persistence of the two-phase domain structure in the melt and the extra energy required to disrupt this structure during flow. If the styrene content is held constant, the total molecular weight has little or no effect on the modulus of the material at ambient temperatures. This is attributed to the modulus of the elastomer phase being inversely proportional to the molecular weight between entanglements in the elastomer chains and the fact that this quantity is not affected by the total molecular weight.

**Proportion of Hard Segments.** As expected, the modulus of styrenic block copolymers increases with the proportion of the hard polystyrene segments. The tensile behavior of otherwise similar block copolymers with a wide range of polystyrene contents shows a family of stress–strain curves (4,7,8). As the styrene content is increased, the products change from very weak, soft, rubberlike materials to strong elastomers, then to leathery materials, and finally to hard glassy thermoplastics. The latter have been commercialized as clear, high impact polystyrenes under the trade name K-Resin (39) (Phillips Petroleum Co.). Other types of thermoplastic elastomers show similar behavior; that is, as the ratio of the hard to soft phase is increased, the product in turn becomes harder.

**Elastomer Segment.** The choice of elastomer segment has a profound effect on the properties of styrenic block copolymers. Four are commercially important: polybutadiene [9003-17-2], polyisoprene [9003-31-0], poly(ethylene-co-butylene) [9019-29-8], and poly(ethylene-co-propylene). The corresponding styrenic triblock copolymers are referred to as S–B–S, S–I–S, S–EB–S, and S–EP–S, respectively. Polybutadiene and polyisoprene both have one double bond per monomer

unit. These double bonds are an obvious source of instability and limit the thermal and oxidative stability of the S–I–S and S–B–S block copolymers. In contrast, poly(ethylene-*co*-butylene) and poly(ethylene-*co*-propylene) are completely saturated, and so S–EB–S and S–EP–S block copolymers are much more stable. Another important aspect is the modulus of the materials. It is postulated that the modulus of these polymers is inversely proportional to the molecular weight between chain entanglements ($M_e$), as well as to the effects of the polystyrene domains acting as reinforcing filler particles (1,40). Values of $M_e$ are as follows (41): polyisoprene (natural rubber), 6100; polybutadiene, 1900; and poly(ethylene-*co*-propylene), 1660. $M_e$ for poly(ethylene-*co*-butylene) is similar to that of poly(ethylene-*co*-propylene) (42). Because of these differences in $M_e$, S–I–S block copolymers are softer than the S–B–S analogues; the S–EB–S and S–EP–S analogues are the hardest.

All these elastomers, especially poly(ethylene-*co*-butylene) and poly(ethylene-*co*-propylene), are nonpolar. The corresponding block copolymers can thus be compounded with hydrocarbon-based extending oils, but do not have much oil resistance. Conversely, block copolymers with polar polyester or polyether elastomer segments have little affinity for such hydrocarbon oils and so have better oil resistance.

Among the polyurethane, polyester, and polyamide thermoplastic elastomers, those with polyether-based elastomer segments have better hydrolytic stability and low temperature flexibility, whereas polyester-based analogues are tougher and have the best oil resistance (43). Polycaprolactones and aliphatic polycarbonates, two special types of polyesters, are used to produce premium-grade polyurethanes (12).

In the hard polymer/elastomer combinations, the elastomer is often chosen to be a polar rubber or it is cross-linked; in some cases it is both. Either of these features improves the resistance to oils and solvents (44).

**Hard Segment.** The choice of the hard segment determines the upper service temperature and also influences the solvent resistance. In styrenic block copolymers, those based on poly(α-methylstyrene) [*25014-31-7*] have higher upper service temperature and tensile strength than analogues based on polystyrene [*9003-53-6*] (7); both are soluble in common solvents. Replacing the polystyrene end segments in S–EB–S by polyethylene (giving E–EB–E block copolymer) improves solvent resistance; the phases are not separated in the melt (7).

In thermoplastic polyurethanes, polyesters, and polyamides, the crystalline end segments, together with the polar center segments, impart good oil resistance and high upper service temperatures. The hard component in most hard polymer/elastomer combinations is crystalline and imparts resistance to solvents and oils, as well as providing the products with relatively high upper service temperatures.


## Synthesis

Block copolymers are synthesized by a variety of methods (45,46); most important are sequential polymerization and step growth. In sequential polymerization, a polymer (A)$_n$ is first synthesized in such a way that it contains at least one group per molecule that can initiate polymerization of another monomer B.

$$A + A + A \ldots \longrightarrow A_n$$
$$A_n + B + B + B \ldots \longrightarrow A_n - B_m$$
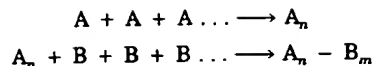
The product can be converted to a triblock copolymer by further addition of A:

$$A_n - B_m + A + A + A \longrightarrow A_n - B_m - A_n$$
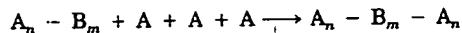
In a variation of this process, polymerization can start in the center $(B_m)$ segment, and $A_n$ segments can then be polymerized onto each end. Alternatively, $A_n - B_m$ can be joined together by a coupling agent:

$$2 A_n - B_m + X \longrightarrow A_n - B_m - X - B_m - A_n$$
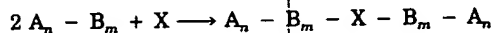
In this example, X is difunctional and the product is linear. If the functionality of X is higher, the product is branched, ie, it is a star polymer.

In step-growth polymerization, one or both segments can be produced separately as difunctional prepolymers. The products can then be linked together:

$$A_n + B_m + A_n + B_m + \ldots \longrightarrow A_n - B_m - A_n - B_m \cdots$$
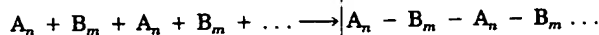
or react with more difunctional monomer:

$$A_n + mB + mC \longrightarrow A_n - (BC)_m - A_n - (BC)_m \cdots$$
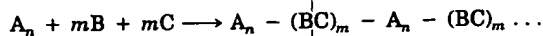
Thermoplastic elastomers that are hard polymer/elastomer combinations are often not truly synthesized. Instead, the two polymers that form the hard and soft phases are intimately mixed on high shear equipment.

## Commercial Production

Commercially, the poly(styrene-*b*-elastomer-*b*-styrene) materials are made by anionic polymerization (7,45–47). An alkyllithium initiator (RLi) first reacts with styrene [100-42-5] monomer:

$$R^-Li^+ + CH_2{=}CH \longrightarrow RCH_2CH^-Li^+$$
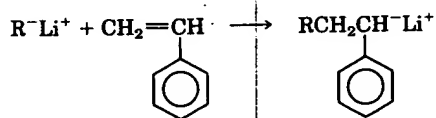
This product acts as an initiator for further polymerization:

$$RCH_2CH^-Li^+ + nCH_2{=}CH \longrightarrow R(CH_2CH)_nCH_2CH^-Li^+$$
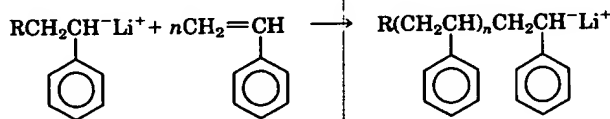
The product, referred to here as $S^-Li^+$, is able to initiate further polymerization. Similar products have been termed living polymers (48). Addition of a second monomer, such as butadiene [106-99-0], gives

$$S^-Li^+ + nCH_2{=}CH{-}CH{=}CH_2 \longrightarrow S{-}(CH_2CH{=}CHCH_2)_{(n-1)}CH_2CH{=}CH{-}CH_2^-Li^+$$
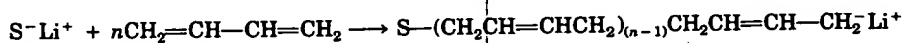
The product of this reaction $(S{-}B^-Li^+)$ may initiate a further reaction with styrene monomer to give $S{-}B{-}S^-Li^+$. This, in turn, can react with an alcohol, ROH,

to give S–B–SH + LiOR. Alternatively, S–B⁻Li⁺ may react with a coupling agent such as an organohalogen (45):

$$2\,\text{S}-\text{B}^-\text{Li}^+ + \text{ClCH}_2-\hspace{-2pt}\bigcirc\hspace{-2pt}-\text{CH}_2\text{Cl} \longrightarrow \text{S}-\text{B}-\text{CH}_2-\hspace{-2pt}\bigcirc\hspace{-2pt}-\text{CH}_2-\text{B}-\text{S} + 2\,\text{LiCl}$$
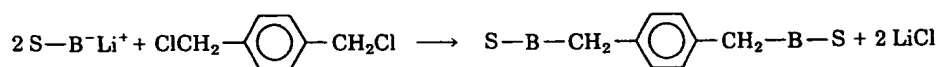
Other coupling agents include esters (45), chlorosilanes (45,46), and divinylbenzene (46). The last gives highly branched materials, whereas the others can give branched or linear products, depending on the functionality of the coupling agent. Another variation of anionic polymerization uses multifunctional initiators (48), in which the polymer chains grow outward from the center of the molecule. In the case considered here, a difunctional initiator (LiRLi) first reacts with butadiene monomer:

$$\text{Li}^{+\,-}\text{R}^-\text{Li}^+ + \text{CH}_2\!\!=\!\!\text{CH}-\text{CH}\!\!=\!\!\text{CH}_2 \longrightarrow \text{Li}^{+\,-}\text{B}-\text{R}-\text{B}^-\text{Li}^+$$

This product is a difunctional initiator and can polymerize styrene monomer:

$$\text{Li}^{+\,-}\text{B}-\text{R}-\text{B}^-\text{Li}^+ + n\text{CH}_2\!\!=\!\!\underset{\bigcirc}{\text{CH}} \longrightarrow \text{Li}^{+\,-}\text{S}-\text{B}-\text{R}-\text{B}-\text{S}^-\text{Li}^+$$
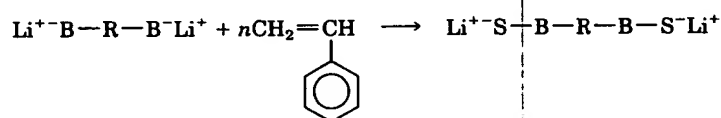
and the final product can again react with an alcohol to give S–B–S, ignoring the minor amount of R moiety at the center of the molecule.

All these polymerizations proceed only in the absence of oxygen or water, which react with the highly reactive propagating species. Polymerization is usually carried out in an inert, hydrocarbon solvent and under a nitrogen blanket. Under these conditions, polymers with narrow molecular-weight distributions and precise molecular weights can be produced in stoichiometric amounts.

Commercially, anionic polymerization is limited to three monomers: styrene, butadiene, and isoprene [78-79-5]; therefore only two useful A–B–A block copolymers, S–B–S and S–I–S, can be produced directly. In both cases, the elastomer segments contain double bonds which are reactive and limit the stability of the product. To improve stability, the polybutadiene mid-segment can be polymerized as a random mixt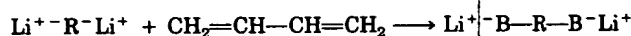ure of two structural forms, the 1,4 and 1,2 isomers, by addition of an inert polar material to the polymerization solvent; ethers and amines have been suggested for this purpose (46). Upon hydrogenation, these isomers give a copolymer of ethylene and butylene.

$$-\text{CH}_2-\text{CH}\!\!=\!\!\text{CH}-\text{CH}_2-\!\!\mid\!\!-\text{CH}_2-\underset{\underset{\text{CH}_2}{\overset{\|}{\text{CH}}}}{\text{CH}}- \overset{\text{H}_2}{\longrightarrow} -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\!\!\mid\!\!-\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\text{CH}}-$$

1,4    1,2          E        B
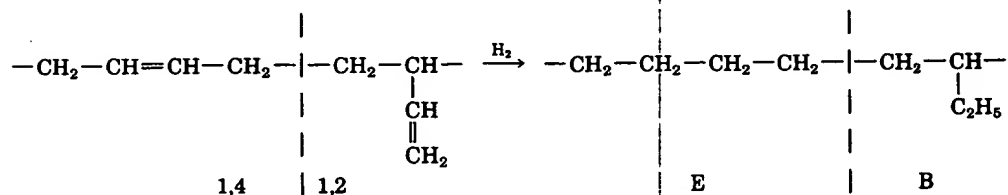
The S–EB–S block copolymers produced in this way have excellent resistance to degradation (49). Similarly, S–I–S block copolymers can be hydrogenated to give the more stable S–EP–S equivalents.

Thermoplastic polyurethane elastomers are produced from prepolymers by polycondensation (12,13). A relatively high molecular-weight polyester or polyether with terminal hydroxy groups (a polyglycol) first reacts with an excess of a diisocyanate.

$$HOR_1OH + 2\ OCNR_2NCO \longrightarrow OCNR_2NHCOOR_1OOCNHR_2NCO$$
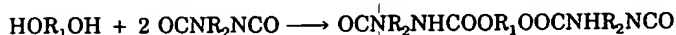
Depending on the excess diisocyanate, this product reacts further with more polyglycol to give a prepolymer in which the segments originally derived from the polyether or polyester glycol and the urethane alternate, and which is terminated by isocyanate groups. This prepolymer, designated $OCNR_3NCO$, becomes the elastomeric or soft segment in the final polymer. It, in turn, reacts with a low molecular-weight glycol such as butanediol and with more diisocyanate.

$$OCNR_3NCO + HO(CH_2)_4OH + OCNR_2NCO \longrightarrow$$

prepolymer

$$-[OOCNHR_3NHCOO(CH_2)_4OOCNHR_2NHCOO(CH_2)_4]_n-$$

soft rubbery segment      hard crystalline segment

The segments derived from the condensation reaction of the butanediol and the diisocyanate agglomerate into separate phases, which a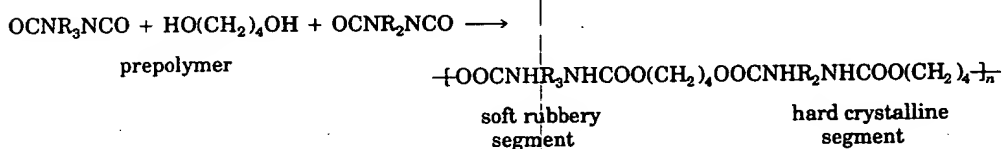re hard and crystalline. The elastomeric chains are thus cross-linked to form a network similar in many ways to that given by the simple poly(styrene-*b*-elastomer-*b*-styrene) polymer described previously (4,5,11). However, the polymer is a multiblock $(A–B)_n$ rather than a simple A–B–A triblock, and the molecular weights and molecular-weight distributions of the segments are not as well controlled. 4,4'-Diphenylmethane diisocyanate is the most common diisocyanate used in this application (13) but toluene and *para*-phenylene (50) diisocyanates are alternatives.

Commercial thermoplastic polyesters are synthesized in a similar way by the reaction of a relatively high molecular-weight polyether glycol with butanediol and dimethyl terephthalate (14,15). The polyether chain becomes the soft segment in the final product, whereas the terephthalic acid–butanediol copolymer forms the hard crystalline domains.

There are several types of thermoplastic polyamides (18). Their synthesis is similar to that of the polyurethane and polyester equivalents (16–18). In some cases, only the soft segments are prepolymers; whereas in others, prepolymers are used to give both segmental types. Both polyesters and polyethers are used for the soft segments, and this choice affects the final properties of the product. Various polyamides, including those based on aromatic groups, may be used for the hard segments. These all have different melting points and degrees of crystallinity and so give products with a wide range of properties.

Information on the synthesis of the polyetherimide–polysiloxane block copolymers has not been disclosed. Many other synthetic methods for preparing block copolymers have been described (19,20,25) but are currently not believed to be commercially important.

The production of the hard polymer/elastomer combinations is more simple. The two-components-are mixed together under conditions of intensive shear. In some cases, grafting may occur. In a variation of this technique, the elastomer can be cross-linked while the mixing is taking place, a process described as dynamic vulcanization (32).

A large number of hard polymer/elastomer combinations made by the last technique have been investigated (30). In some cases, the components are technologically compatibilized by use of a grafting reaction, but usually a fine dispersion of the two phases is formed that is sufficient to give the product the properties of a thermoplastic elastomer.

## Economic Aspects

Global consumption of thermoplastic rubbers of all types is estimated at about 600,000 t/yr (51). Of this, 42% was estimated to be consumed in the United States, 39% in Western Europe, and 19% in Japan. At present, the worldwide market is estimated to be divided as follows: styrenic block copolymers, 48%; hard polymer/elastomer combinations, 26%; thermoplastic polyurethanes, 12%; thermoplastic polyesters, 4%; and others, 9%. The three largest end uses were transportation, 23%; footwear, 18%; and adhesives, coatings, etc, 16%. The ranges of the hardness values, prices, and specific gravities of commercially available materials are given in Table 4.

**Table 4.** Price and Property Ranges for Thermoplastic Elastomers[a]

| Elastomer | Approximate price range, $/kg | Specific gravity | Hardness range[b] |
|---|---|---|---|
| polystyrene/elastomer block copolymers | | | |
|   S–B–S (pure) | 1.9–2.6 | 0.94 | 65A–75A |
|   S–I–S (pure) | 2.2–2.9 | 0.92 | 32A–37A |
|   S–EB–S (pure) | 4.1–5.9 | 0.91 | 65A–75A |
|   S–B–S (compounds) | 1.3–3.1 | 0.9–1.1* | 40A–45D |
|   S–EB–S (compounds) | 2.4–4.4 | 0.9–1.2 | 18A–60D |
| polyurethane/elastomer block copolymers | 4.4–7.2 | 1.05–1.25 | 70A–75D |
| polyester/elastomer block copolymers | 4.6–7.7 | 1.15–1.40 | 35D–70D |
| polyamide/elastomer block copolymers | 7.5–8.8 | 1.0–1.15 | 60A–65D |
| polyetherimide/polysiloxane block copolymers | 37 | 1.18 | 70D |
| polypropylene/EPDM or EPR blends | 2.0–3.3 | 0.9–1.05 | 60A–65D |
| polypropylene/EPDM dynamic vulcanizates | 3.6–5.5 | 0.95–1.0 | 45A–50D |
| polypropylene/butyl rubber dynamic vulcanizates | 4.6–7.9 | 0.95–1.0 | 40A–80A |
| polypropylene/natural rubber dynamic vulcanizates | 2.6–3.5 | 1.0–1.05 | 60A–50D |
| polypropylene/nitrile rubber dynamic vulcanizates | 4.4–5.5 | 1.0–1.1 | 70A–50D |
| PVC/nitrile rubber blends | 2.9–3.1 | 1.20–1.33 | 50A–80A |
| halogenated polyolefin/ethylene interpolymer blends | 3.5–4.4 | 1.10–1.25 | 60A–80A |

[a]These price and property ranges do not include fire retardant grades or highly filled materials for sound deadening.
[b]Shore A or D as indicated.

## Applications

Trade names and suppliers of commercial thermoplastic elastomers of all types are given in Tables 5–7.

**Styrenic Block Copolymers.** The applications of these block copolymers are described in detail in Reference 6.

**Table 5.** Trade Names of Thermoplastic Elastomers Based on Styrenic Block Copolymers[a]

| Trade name | Manufacturer | Type | Elastomer segment | Notes |
|---|---|---|---|---|
| *General-purpose, soluble*[b] | | | | |
| Kraton D and Cariflex | Shell | linear and branched | B or I | also compounded products |
| Vector[c] | Dexco | linear | B or I | |
| Solprene[d] | Phillips | branched | B | |
| Finaprene | Fina | linear | B | |
| .fprene and Asaprene | Asahi | linear | B | |
| _ uroprene Sol T | Enichem | linear and branched | B or I | |
| Quintac | Nippon Zeon | linear | I | |
| Kraton G | Shell | linear | EB or EP | improved stability |
| Dynaflex | GLS[e] | linear | B or EB | only compounded products |
| Elexar | Shell[f] | linear | EB | wire and cable compounds |
| Flexprene | Teknor Apex | linear | B ⎫ | only compounded products |
| Tekron | Teknor Apex | linear | EB ⎭ | |
| Septon | Kuraray | linear | EP | elastomer block is hydrogenated polyisoprene |
| C-Flex | Concept | linear | EB | medical applications; contains silicone oil |
| *Specialty materials* | | | | |
| Stereon | Firestone | linear | B | high polystyrene content |
| K-Resin | Phillips | branched | B | very high polystyrene content; hard and rigid |

[a]Hard segment = styrene.
[b]Not available as compounded products unless otherwise noted.
[c]Joint venture of Dow and Exxon.
[d]No longer made in the United States.
[e]Great Lakes Terminal and Transport Corp.
[f]Now produced by Teknor Apex Co.

**Table 6. Trade Names of Multiblock Thermoplastic Elastomers Based on Polyurethane/Elastomer, Polyether/Elastomer, and Polyamide/Elastomer Block Copolymers**

| Trade name | Manufacturer | Hard segment | Elastomer segment | Notes |
|---|---|---|---|---|
| Estane<br>Q-Thane[a]<br>Pellethane[a]<br>Texin<br>Elastollan | B. F. Goodrich<br>Morton International<br>Dow<br>Miles[b]<br>BASF | polyurethane | polyether or polyester (amorphous) | hard, abrasion- and oil-resistant; high cost |
| Urafil<br>Hytrel<br>Lomod<br>Ecdel<br>Riteflex | Akzo<br>Du Pont<br>GE<br>Eastman<br>Hoechst-Celanese | polyester | polyether | similar to polyurethane and better at low temperatures |
| Pebax<br>Vestenamer<br>Grilamid<br>Montac[c]<br>Orevac[c] | Atochem<br>Hüls<br>Emser<br>Monsanto<br>Atochem | polyamide | polyether or polyester (amorphous) | similar to polyurethanes but can be softer; very good at low temperatures |
| Siltem | GE | polyether imide | polysiloxane | fire retardant; used in wire and cable insulation |

[a]Including some with polycaprolactone segments.
[b]Formerly Mobay. Includes some polymers with aliphatic polycarbonate segments (trade named: Desmopan).
[c]For hot-melt adhesives.

*Substitute for Conventional Vulcanized Rubbers.* For this application, the products are processed by techniques and equipment developed for conventional thermoplastics, ie, injection molding, extrusion, etc. The S–B–S and S–EB–S polymers are preferred (small amounts of S–EP–S are also used). To obtain a satisfactory balance of properties, they must be compounded with oils, fillers, or other polymers; compounding reduces costs. Compounding ingredients and their effects on properties are given in Table 8. Oils with high aromatic content should be avoided because they plasticize the polystyrene domains. Polystyrene is often used as an ingredient in S–B–S-based compounds; it makes the products harder and improves their processibility. In S–EB–S-based compounds, crystalline polyolefins such as polypropylene and polyethylene are preferred. Some work has been reported on blends of liquid polysiloxanes with S–EB–S block copolymers. The products are primarily intended for medical and pharmaceutical-type applications and hardnesses as low as 5 on the Shore A scale have been reported (53).

Large amounts of inert fillers, such as whiting, talc, and clays, can be added. Very dense fillers, such as barium or strontium sulfates, are used to make compounds intended for sound-deadening applications. In contrast, high levels of reinforcing fillers, such as carbon black, produce undesirable properties in the final product.

**Table 7. Some Trade Names of Thermoplastic Elastomers Based on Hard Polymer/Elastomer Combinations**

| Trade name | Manufacturer | Type | Elastomer | Notes |
|---|---|---|---|---|
| *Polypropylene hard polymer* | | | | |
| TPR | AES[a] | blend | EPDM or EPR | relatively hard, low density, not highly filled |
| Ren-Flex | Dexter | | | |
| Polytrope | Schulman | | | |
| Telcar | Teknor Apex | | | |
| Ferroflex | Ferro | | | |
| Hifax | Himont | | | |
| Santoprene | AES | DV[b] | EPDM | better oil resistance, low compression set, softer |
| Sarlink 3000 | Novacor | | | |
| Telprene | Teknor Apex | | | |
| Hifax XL | Himont | | | |
| Trefsin | AES | DV | butyl rubber | low permeability, high damping |
| Sarlink 2000 | Novacor | DV | | |
| Vyram | AES | DV | natural rubber | low cost |
| Geolast | AES | DV | nitrile rubber | oil-resistant |
| *Poly(vinyl chloride) hard polymer* | | | | |
| Sarlink 1000 | Novacor | DV | nitrile rubber | oil-resistant |
| Chemigum | Goodyear | blend | | |
| Ultraprene | Teknor Apex | blend | | |
| Elastar | Nippon Zeon | c | | |
| *Other hard polymers* | | | | |
| Alcryn | Du Pont | blend[d] | ethylene interpolymer | single-phase, soft, oil-resistant |
| Rimplast | Petrarch Systems | blend[e] | | medical applications |

[a] Advanced Elastomer Systems; a joint venture between Monsanto and Exxon.
[b] The soft phase is dynamically vulcanized, ie, cross-linked during mixing (32).
[c] Elastomer phase reported to be ionically cross-linked (52).
[d] Chlorinated polyolefin hard polymer.
[e] Blend of other thermoplastic elastomers with silicone rubbers.

A large volume usage of S–B–S-based compounds is in footwear. Canvas footwear, such as sneakers and unit soles, can be made by injection molding. Frictional properties resemble those of conventionally vulcanized rubbers and are superior to those of the flexible thermoplastics, such as plasticized poly(vinyl chloride). The products remain flexible under cold conditions because of the good low temperature properties of the polybutadiene segment.

Compounds based on S–EB–S usually contain polypropylene, which improves solvent resistance and processibility and raises upper service temperatures. Compounds intended for use in the automotive industry are able to survive

**Table 8.** Compounding Styrenic Block Copolymers

| Properties | Component | | | | |
| --- | --- | --- | --- | --- | --- |
| | Oils | Polystyrene | Polyethylene | Polypropylene | Fillers |
| hardness | decreases | increases | increases | increases | small increase |
| processibility | improves | improves | improves | improves, especially with S–EB–S | improves |
| effect on oil resistance | none | none | improves | improves | none |
| cost | decreases | decreases | decreases | decreases | decreases |
| other | decreases uv resistance | | often gives satin finish | improves high temperature properties | often improves surface appearance |

1000 hours air exposure at temperatures of 125°C with only minor changes in properties (54). Very soft compounds have been developed to replace foam rubber for interior trim parts. In this and similar applications, these soft compounds are usually insert molded over polypropylene or metal and then coated with flexible polyurethane paint (55). Other automotive applications include products intended for sound deadening, flexible air ducts, and gear shifter boots, as well as improving the properties of sheet molding compounds.

Other uses for which special compounds have been developed include materials intended for food contact, wire insulation, and pharmaceutical applications.

Commercial products have hardnesses from 28 on the Shore A scale (which is very soft) to 45 on the Shore D scale (almost leathery). Specific gravities usually range from 0.9 to 1.20; some products intended for soundproofing have specific gravities as high as 1.95. Properties of representative grades are given in Table 9.

Processing is relatively easy. In general, products based on S–B–S are processed under conditions appropriate for polystyrene, whereas products based on S–EB–S are processed under conditions appropriate for polypropylene. Pre-drying is not needed and scrap is recycled.

*Adhesives, Coatings, and Sealants.* For these applications, styrenic block copolymers must be compounded with resins and oils (Table 10) to obtain the desired properties (56–58). Materials compatible with the elastomer segments soften the final product and give tack, whereas materials compatible with the polystyrene segments impart hardness. The latter are usually styrenic resins with relatively high softening points. Materials with low softening points are to be avoided, as are aromatic oils, since they plasticize the polystyrene domains and reduce the upper service temperature of the final products.

These resins and oils have low molecular weights, ie, typically below 1000. This, combined with the relatively low molecular weights of the styrenic block copolymers, ie, 30,000–150,000, allows solutions in common solvents to be formulated at high solids levels. Alternatively, the products can be applied as hot

**Table 9. Properties of Compounded Styrenic Block Copolymers**

| Product | Kraton D2109 | Kraton G2705 | Dynaflax D3202[a] | Kraton D5119 | Kraton D5298 | Kraton G7535X | Kraton G7528X | Kraton G7702 | Kraton G7715 | Kraton G7720 | Elexar 8431 | Elexar 8451 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| application | milk tubing | medical general-purpose | general-purpose | footwear unitsole | footwear slipper-sole | soft function-alized | automotive very soft | automotive low compres-sion set | automotive general-purpose | automotive general-purpose | wire and cable | wire and cable |
| | | | | | | *Properties* | | | | | | |
| hardness, Shore A or D | 48A[b] | 55A | 50A | 55A | 47A | 35A | 28A | 36A | 57A | 60A | 64A | 82A[b]/34D |
| tensile strength, MPa[c] | 11[b] | 6.0 | 5.6 | 3.8 | 3.9 | 7.0 | 5.8 | 4.6 | 12[b] | 5.0 | 9.6[b] | 12[b] |
| 300% modulus, MPa[c] | 2.0[b] | 2.8 | 4.3 | 3.5 | 1.9 | 1.3 | 1.0 | 3.2 | 2.6[b] | 2.5 | 3.6[b] | 4.4[b] |
| elongation, % | 850[b] | 700 | 400 | 360 | 550 | 900 | 950 | 650 | 750[b] | 700 | 650[b] | 650[b] |
| specific gravity | 0.94 | 0.90 | 1.0 | 1.09 | 0.96 | 0.92 | 0.91 | 1.07 | 0.91 | 1.19 | 0.92 | 1.01 |

[a]Formerly Kraton D3202.
[b]Measured on extruded samples, all others measured on injection molded samples.
[c]To convert MPa to psi, multiply by 145.

30

**Table 10. Resins Used to Formulate Adhesives, Sealants, Etc From Styrenic Block Copolymers**

| Resin type | Segment compatibility[a] |
|---|---|
| polymerized $C_5$ resins (synthetic polyterpenes) | I |
| hydrogenated rosin esters | B |
| saturated hydrocarbon resins | EB |
| naphthenic oils | I, B |
| paraffinic oils | EB |
| low molecular-weight polybutenes | EB |
| aromatic resins | S |

[a] I indicates compatible with polyisoprene segments; B, compatible with polybutadiene segments; EB, compatible with poly(ethylene–butylene) segments; and S, compatible with polystyrene segments.

melts, with considerable advantages in terms of safety, production rates, energy consumption, and air pollution.

*Blends with Thermoplastics or Other Polymeric Materials.* Styrenic block copolymers are technologically compatible with a surprisingly wide range of materials and can be blended to give useful products (59). Blending can often be carried out on the equipment producing the final article. Blends of S–B–S with polystyrene, polyethylene, or polypropylene show improved impact and tear resistance. Similarly, S–EB–S can be blended with the less polar engineering thermoplastics such as poly(phenylene oxide) and polycarbonate. An unusual feature of these block copolymers is their ability to enable useful blends to be made from incompatible polymers, eg, polystyrene or poly(butylene terephthalate) with polyethylene (60). A new development is the use of functionalized S–EB–S block copolymers as impact modifiers for more polar engineering thermoplastics such as polyesters and polyamides. The functionality is given by maleic acid/anhydride groups grafted to the S–EB–S polymer chain. These functionalized S–EB–S block copolymers have also been found useful in the compatibilization of polyolefins with polyamides (61) and with poly(phenylene ether) (62).

Special grades of styrenic block copolymers are useful modifiers for sheet molding compounds (SMC) based on thermoset polyesters. They improve surface appearance, impact resistance, and hot strength.

Blends with styrenic block copolymers improve the flexibility of bitumens and asphalts. The block copolymer content of these blends is usually less than 20%; even as little as 3% can make significant differences to the properties of asphalt (qv). The block copolymers make the products more flexible, especially at low temperatures, and increase their softening point. They generally decrease the penetration and reduce the tendency to flow at high service temperatures; and they also increase the stiffness, tensile strength, ductility, and elastic recovery of the final products. Melt viscosities at processing temperatures remain relatively low so the materials are still easy to apply. As the polymer concentration is increased to about 5%, an interconnected polymer network is formed. At this point the nature of the mixture changes from an asphalt modified by a polymer to a polymer extended with an asphalt.

It is important to choose the correct grade of asphalt; those with a low asphaltene content and/or high aromaticity in the maltene fraction usually give the best results (63,64). Applications include road surface dressings such as chip seals (applied to hold the aggregate in place when a road is resurfaced); slurry seals; hot-mix asphalt concrete (a mixture of asphalt and aggregate used in road surfaces); road crack sealants; roofing; and other waterproofing and adhesive applications (64–66). Because of their lower cost, S–B–S block copolymers are usually chosen for this application; but in roofing and paving applications, the S–EB–S block copolymers are also used because of better long-term aging resistance.

**Multiblock Copolymers.** Replacement of conventional vulcanized rubber is the main application for the polar polyurethane, polyester, and polyamide block copolymers. Like styrenic block copolymers, they can be molded or extruded using equipment designed for processing thermoplastics. Melt temperatures during processing are between 175 and 225°C, and predrying is required; scrap is reusable. They are mostly used as essentially pure materials, although some work on blends with various thermoplastics such as plasticized and unplasticized PVC and also ABS and polycarbonate (14,18,67–69) has been reported. Plasticizers intended for use with PVC have also been blended with polyester block copolymers (67).

All three types of these block copolymers are relatively hard (from 70 on the Shore A scale to 70 on the Shore D scale) with specific gravities of 1.00–1.25. Properties of individual grades have been described in detail (Tables 11–13). Applications (13,15,18) taking advantage of toughness, abrasion resistance, flexibility, and resistance to oils and solvents include belting, hydraulic hose, tires, shoe soles, wire coatings, and automobile parts. The surface of these molded parts can be easily painted or metallized. Medical uses, such as implants, are a significant application for the polyurethane block copolymers with polyether elastomer segments (70). Blends with silicone rubbers have been described for these applications (37,38). Another application is the use of a clear polyester thermoplastic elastomer as a replacement for glass bottles in medical applications (3).

Some grades of polyurethane and polyester copolymers are used as hot-melt adhesives. Applications include shoe manufacture and as an adhesive interlayer in coextrusion.

**Table 11.** Properties of Polyurethane/Elastomer Block Copolymers

| Product | Estane 58133 | Estane 58311 | Q-Thane PC86 | Texin 480A | Pellethane 2102-90A | Pellethane 2103-70A |
|---|---|---|---|---|---|---|
| soft segment type | polyester | polyether | polyester | polyester | polycapro-lactone | polyether |
| hardness, Shore A or D | 55D | 85A | 50D | 86A | 90A | 70A |
| tensile strength, MPa[a] | 40 | 47 | 52 | 41 | 48 | 24 |
| 100% modulus, MPa[a] | 14 | 6.2 | 8.3 | 5.1 | 10.7 | 3.5 |
| elongation, % | 500 | 530 | 475 | 500 | 500 | 500 |
| specific gravity | 1.22 | 1.11 | | 1.20 | 1.20 | 1.06 |

[a]To convert MPa to psi, multiply by 145.

**Table 12. Properties of Polyester/Elastomer Block Copolymers**

| Product | Hytrel 4056 | Hytrel 5526 | Hytrel 6356 | Hytrel 7246 | Lomod ST3090A | Lomod TE3055A |
|---|---|---|---|---|---|---|
| hardness, Shore A or D | 40D 92A | 55D | 63D | 72D | 90A 31D | 54D |
| tensile strength, MPa[a] | 26 | 40 | 41 | 46 | .14 | 23 |
| 100% modulus, MPa[a] | 9.5 | 19 | 20[b] | 25[b] | | |
| elongation, % | 550 | 500 | 420 | 350 | 250 | 290 |
| specific gravity | 1.17 | 1.20 | 1.22 | 1.25 | 1.13 | 1.22 |

[a]To convert MPa to psi, multiply by 145.
[b]After yielding at lower elongation.

**Table 13. Typical Properties of Polyamide/Elastomer and Polyetherimide/Elastomer Block Copolymers**

| Product | Pebax 2533 | Pebax 4033 | Pebax 6333 | Grilamid Ely 60 | Siltem[a] STM1500 |
|---|---|---|---|---|---|
| hardness, Shore A or D | 25D 75A | 40D | 63D | 62D | 69D |
| tensile strength, MPa[b] | 29 | 33 | 49 | 36 | 25 |
| 100% modulus, MPa[b] | 4.3 | 10 | 19 | | |
| elongation, % | 350 | 620 | 680 | 300 | 105 |
| specific gravity | 1.01 | 1.01 | 1.01 | 1.01 | 1.18 |

[a]Fire retardant grade; intended for wire insulation.
[b]To convert MPa to psi, multiply by 145.

The polyetherimide–polysiloxane multiblock copolymers are relatively hard (about 70 on the Shore D scale). Their main application is flame-resistant wire and cable covering (24), where they combine very low flammability with a low level of toxic products in the smoke. This unusual and vital combination of properties justifies their relatively high price, about $37/kg, at a specific gravity of about 1.2.

**Hard Polymer/Elastomer Combinations.** Substitution of conventional vulcanized rubbers is the main application for these materials (27,28,31). The first ones to be developed were those based on polypropylene and EPDM. To begin with, simple mechanical mixtures of the two components were introduced. These had some limitation, because EPDM in its unvulcanized state has almost no tensile strength or oil resistance. Thus only fairly hard products, ie, those containing small amounts of EPDM, had satisfactory properties and so the first products of this type had hardness values in the Shore D range, although softer versions are now available. In later work, products based on dynamic vulcanization (32) were produced. In this process, the EPDM is simultaneously mixed and cross-linked. The result is a very fine dispersion of vulcanized EPDM particles in a polypropylene matrix. The improved properties of the EPDM phase allow much higher levels to be used, giving quite soft products (as low as about 45 on the Shore A

scale). Compared to the mixtures of EPDM with polypropylene, the dynamic vulcanizates have lower compression set and better oil resistance. Natural and butyl rubbers have been used to replace EPDM in similar dynamically vulcanized products (33,34). Those based on natural rubber are low in cost and have properties intermediate between the EPDM-based dynamic vulcanizates and the simple EPDM-based mixtures. Those based on butyl rubber have low gas permeability and high damping, thus they are often used as vapor barriers or vibration isolators. An unexpected property advantage with those based on butyl rubber is that some grades show excellent adhesion when insert molded against such polar engineering thermoplastics as poly(butylene terephthalate) and polyamides (71). Hardness values are between about 60 and 80 on the Shore A scale. Specific gravities of these various combinations of polypropylene with EPDM, butyl, and natural rubbers are between about 0.9 and 1.05. Properties of representative grades are given in Table 14. Molding and extrusion conditions are similar to those used for polypropylene, and the scrap is reusable. Important applications are wire insulation, appliance parts, and automobile exterior and interior parts (both painted and unpainted).

Even though vulcanized EPDM has some oil resistance, in contrast to unvulcanized EPDM which has virtually none, a rubber with inherent oil resistance should be even better. For this reason, more polar rubbers have replaced EPDM in applications where oil resistance is critical. Dynamic vulcanizates of nitrile rubber with polypropylene are one example. Commercial grades are somewhat harder than EPDM equivalents (between 70 on the Shore A scale to 40 on the Shore D scale) and are also more dense (about 1.0 to 1.1 specific gravity). PVC/nitrile blends and dynamic vulcanizates also have excellent oil resistance as well as resistance to flex cracking and abrasion (36). Hardness ranges from about 50 to 80 on the Shore A scale and specific gravity from about 1.2 to 1.3. Blends of halogenated polyolefins with ethylene interpolymers are claimed to give single-phase systems (29). They have a very rubberlike feel and are similar to the PVC/nitrile rubber combinations as far as hardness and specific gravity are concerned. Like them, they have good oil resistance. All these products based on the more polar rubbers are used in molded appliance, automotive, and similar rubberlike parts where oil resistance is needed at a reasonable cost. Properties of representative grades are given in Table 15.

**Table 14. Properties of Hard Polymer/Elastomer Combinations**

| Product | Vistaflex | | Republic AB 6053[a] | Telcar 302 | Santoprene | | Trefsin 3201-60 |
| | 9101-65-W900 | 9013-45-W900 | | | 101-73 201-73 | 103-40 203-40 | |
|---|---|---|---|---|---|---|---|
| hardness, Shore A or D | 65A | 45D | 45D | 75A | 73A | 40D | 60A |
| tensile strength, MPa[b] | 4.5 | 15 | 4.8 | 11 | 8.3 | 19 | 4.6 |
| 100% modulus, MPa[b] | 2.2 | 11 | | | 3.2 | 8.6 | 1.9 |
| elongation, % | 525 | 750 | 350 | 900 | 375 | 600 | 355 |
| specific gravity | 1.00 | 0.95 | 1.85 | 0.88 | 0.98 | 0.95 | 0.97 |

[a]Grade intended for sound-deadening applications.
[b]To convert MPa to psi, multiply by 145.

**Table 15.** Properties of Hard Polymer/Elastomer Combinations Based on Polar Elastomers

| | Geolast | | Alcryn MPR | | | Sarlink | Chemigum | |
| | | | | | | | 03050/ | 03070/ |
| Product | 701-70 | 701-87 | 60A | 70A | 80A | 1160 | 03150 | 03170 |
|---|---|---|---|---|---|---|---|---|
| hardness, Shore A or D | 70A | 87A | 62A | 69A | 78A | 57A | 50A | 70A |
| tensile strength, MPa$^a$ | 6.2 | 12 | 12 | 13 | 13 | 11 | 12 | 17 |
| 100% modulus, MPa$^a$ | 3.3 | 6.0 | 3.7 | 4.5 | 7.2 | 3.4 | 2.9 | 5.9 |
| elongation, % | 265 | 380 | 325 | 295 | 210 | 345 | 470 | 400 |
| specific gravity | 1.00 | 0.98 | 1.21 | 1.23 | 1.25 | 1.17 | 1.20 | 1.23 |

$^a$To convert MPa to psi, multiply by 145.

## Health and Safety

Most thermoplastic elastomers are stable materials and decompose only slowly under normal processing conditions. If decomposition does occur, the products are usually not particularly hazardous and should not present a problem if good ventilation is provided. Extra caution should be exercised when processing polyurethanes, especially those containing polycaprolactone segments. In these cases the decomposition products may include isocyanates and caprolactam, both of which are potential carcinogens.

Of course, all materials that are processed in the molten state can cause burns if the hot material comes in contact with the skin. Care must be taken to avoid this, and it should be noted that molten material left in the barrel of an extruder or injection molding machine can "spit" unexpectedly. In all cases, it is recommended that the manufacturer's Material Safety Data Sheet be consulted before working with any of these materials.

## Reprocessing

Easy reprocessing is one of the great advantages that thermoplastic elastomers have over conventional vulcanized rubbers. The scrap can be reground and is usually blended with virgin material before being reworked. Regrinding is not difficult if it is remembered that rubber must be cut rather than shattered. This means that the cutter blades must be sharp and clearances minimized. It is usually best to dry the ground scrap before reworking it, and for the polyurethanes, polyesters, and polyamides, drying is a necessity. Thermoplastic elastomers can also be used to "sweeten" regrind; that is, they can be blended with reground scrap from conventional thermoplastics to restore impact strength and reduce brittleness. Many applications, eg, coextrusion, generate mixed scrap, which usually has very poor properties. Thermoplastic elastomers can often convert this into useful material (60–62).

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